



# Mixtures of ionic liquid – Alkylcarbonates as electrolytes for safe lithium-ion batteries

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## HIGHLIGHTS

- Mixture electrolytes composed by alkyl-carbonates and ionic liquid (IL).
- New electrolytes for lithium-ion cells with enhanced safety profile.
- IL-based lithium-ion cell adopting LiFePO<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes.

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## ABSTRACT

Mixtures of alkylcarbonate electrolytes with an ionic liquid (IL) and a lithium salt have been studied in order to develop new electrolytes for lithium-ion cells with enhanced safety profiles. In this work the influence of the addition of *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Py<sub>14</sub>TFSI) on the electrochemical properties of commercial carbonate-based electrolytes, i.e. 1 M LiPF<sub>6</sub> in EC:DMC (LP30) and in EC:DMC:DEC (LP71) is reported. Four new electrolyte compositions have been prepared and characterized.

The addition of the ionic liquid in the electrolyte carbonate-based solution results in (i) an ionic conductivity comparable with that of the pristine IL-free carbonate-based electrolyte, (ii) the enlargement of the electrochemical stability window, and (iii) a large reduction of the self-extinguish time (SET) of the electrolyte mixture when exposed to a free flame.

All the newly developed electrolytes have been tested in lithium cells versus LiFePO<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes: the cells show good performances in galvanostatic cycling. The best performing electrolyte i.e. LP30/Py<sub>14</sub>TFSI 70/30 wt/wt has been also successfully tested in a full Li-ion cell realized by coupling LiFePO<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes.

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## 1. Introduction

Lithium ion batteries are used today in all the popular portable electronic devices, e.g. mobile phones, laptops, and others, thanks to the high energy content compared to any other electrochemical energy storage device. Commonly a lithium ion cell is constituted by a graphite anode, a lithium metal oxide cathode and a separator soaked with a liquid solution of a lithium salt (e.g., lithium-hexafluorophosphate, LiPF<sub>6</sub>) in an organic solvent mixture (e.g., EC–DMC mixture). This kind of batteries is light, compact and has an operational voltage averaging on 3.6 V, with an energy density that, according to the structure, ranges from 150 Wh kg<sup>−1</sup> up to 250 Wh kg<sup>−1</sup> [1,2].

A serious issue in lithium ion cell technology is safety. Electrodes and electrolytes are both hazard factors in Li-ion cells. In particular the use of graphite-based electrodes easily leads to the release upon cycling of gaseous products or even more dangerously to lithium plating on the electrode surface at high current regimes. Substitutes to graphite have been proposed (e.g. titanium oxide, TiO<sub>2</sub>) [3] and incorporated in advanced Li-ion cells [4]. However electrolytes are the most critical component for the control of safety of lithium batteries because of the high vapor pressure and the flammability of the LiPF<sub>6</sub>-organic carbonate solution electrolytes.

One of the best ways to improve safety and reliability of the Li-ion battery electrolytes is the use of an emerging class of electrolytes based on ionic liquids ILs, namely, low temperature molten salts. Typically, ILs are formed by the combination of a weakly interacting, large cation and a flexible anion. ILs are non-volatile,

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**Table 1**

The composition of the electrolyte samples studied in this work.

Sample	Sample name	% of ionic liquid	% of carbonate solution
Py <sub>14</sub> TFSI	IL	100	0
LP30	LP30	0	100
LP30/Py <sub>14</sub> TFSI	LP30/IL-30	30	70
70/30 wt/wt			
LP30/Py <sub>14</sub> TFSI	LP30/IL-50	50	50
50/50 wt/wt			
LP71	LP71	0	100
LP71/Py <sub>14</sub> TFSI	LP71/IL-30	30	70
70/30 wt/wt			
LP71/Py <sub>14</sub> TFSI	LP71/IL-50	50	50
50/50 wt/wt			

non-flammable, highly conductive, environmentally compatible and can safely operate in a wide temperature range. This unique combination of favorable properties makes ILs very appealing materials for stable and safe electrolytes in lithium batteries [5–16]. The substitution of the conventional flammable and volatile organic solutions with ILs is expected to greatly reduce the risk of thermal runaways and, eventually, fire accidents, thus drastically improving the overall safety of the cell. We recently proposed a novel ionic liquid (i.e. *N*-butyl-*N*-ethyl pyrrolidinium *N,N*-bis(trifluoromethanesulfonyl)imide, Py<sub>24</sub>TFSI) containing a suitable lithium salt (i.e. lithium bis(trifluoromethanesulfonyl)imide, LiTFSI) as advanced electrolyte for lithium batteries. This IL-based electrolyte offers a good compatibility with the lithium metal electrode, while maintaining high thermal stability and acceptable conductivity [17]. Very promising performances were also shown in terms of interface stability, cycle life, and rate capability when the Py<sub>24</sub>TFSI–LiTFSI solution was tested in lithium cells [18,19]. We also prepared IL-containing polymer membranes by immobilizing a solution of LiTFSI in Py<sub>24</sub>TFSI mixed with other organic solvents, such as ethylene carbonate, propylene carbonate and dimethyl carbonate (EC, PC, and DMC), into a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix. These gel electrolytes showed promising electrochemical performances [20].

Some interesting examples of mixing ionic liquids with aprotic organic solvents to form hybrid electrolytes have been proposed in literature [21–25]. As an example Guerfi et al. [21] observed that by mixing 1 M LiPF<sub>6</sub> in ethylene carbonate and diethyl carbonate with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquid it is possible to improve the safety without compromising performances. They observed that electrolytes containing 30–40% of IL offer the best compromise between viscosity and ionic conductivity.

In this work we report the characterization of mixed liquid electrolytes made by large addition of an ionic liquid, i.e. Py<sub>14</sub>TFSI, to commercial electrolytes containing a lithium salt dissolved in carbonate-based (ethylene carbonate, dimethyl carbonate and diethyl carbonate) solutions, i.e. 1 M LiPF<sub>6</sub> in EC:DMC 1:1 wt/wt and in EC:DMC:DEC 1:1:1 wt/wt, as well as the performances of lithium half-cells and complete Li-ion cells made with these new electrolytes.

## 2. Experimental

The electrolyte solutions were prepared by mixing different amounts (30% wt. and 50% wt.) of Py<sub>14</sub>TFSI (Solvionic) to both the carbonate-based solutions, i.e. EC:DMC 1:1 wt/wt, 1 M LiPF<sub>6</sub> and EC:DEC:DMC 1:1 wt/wt, 1 M LiPF<sub>6</sub>, LP30 and LP71 respectively (Merck products). Both IL and the commercial battery grade electrolytes (i.e. LP30 and LP71) were used as provided. Details on the composition of the studied samples, i.e. the four mixture electrolytes as well as the pure LP30 and LP71, are summarized in Table 1.

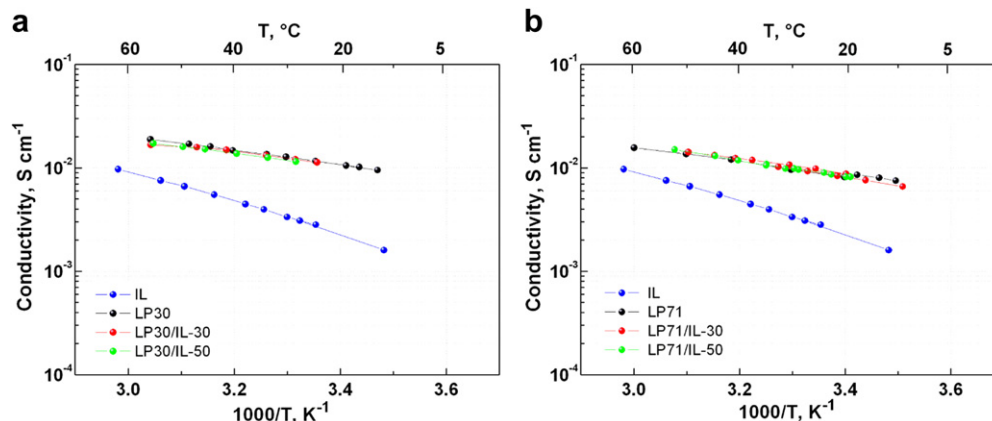
The water content of the ionic liquid was confirmed to be less than 20 ppm according to a standard Karl Fischer titration method (Metrohm KF 831 Coulometer), being this value acceptable for a Li-ion battery grade electrolyte solution [26].

To avoid any contamination with external ambient, all the materials handlings were carried out in a controlled argon atmosphere dry box having a humidity content below 1 ppm.

The ionic conductivity measurements were carried by AC impedance spectroscopy, dipping in the solutions a test cell with platinized platinum blocking electrodes and known cell constant (Amel product). All the measurements were performed in the temperature range from 10 °C to 60 °C. Before each measurement cells were kept at constant temperature for 1 day ca. to reach thermal equilibration.

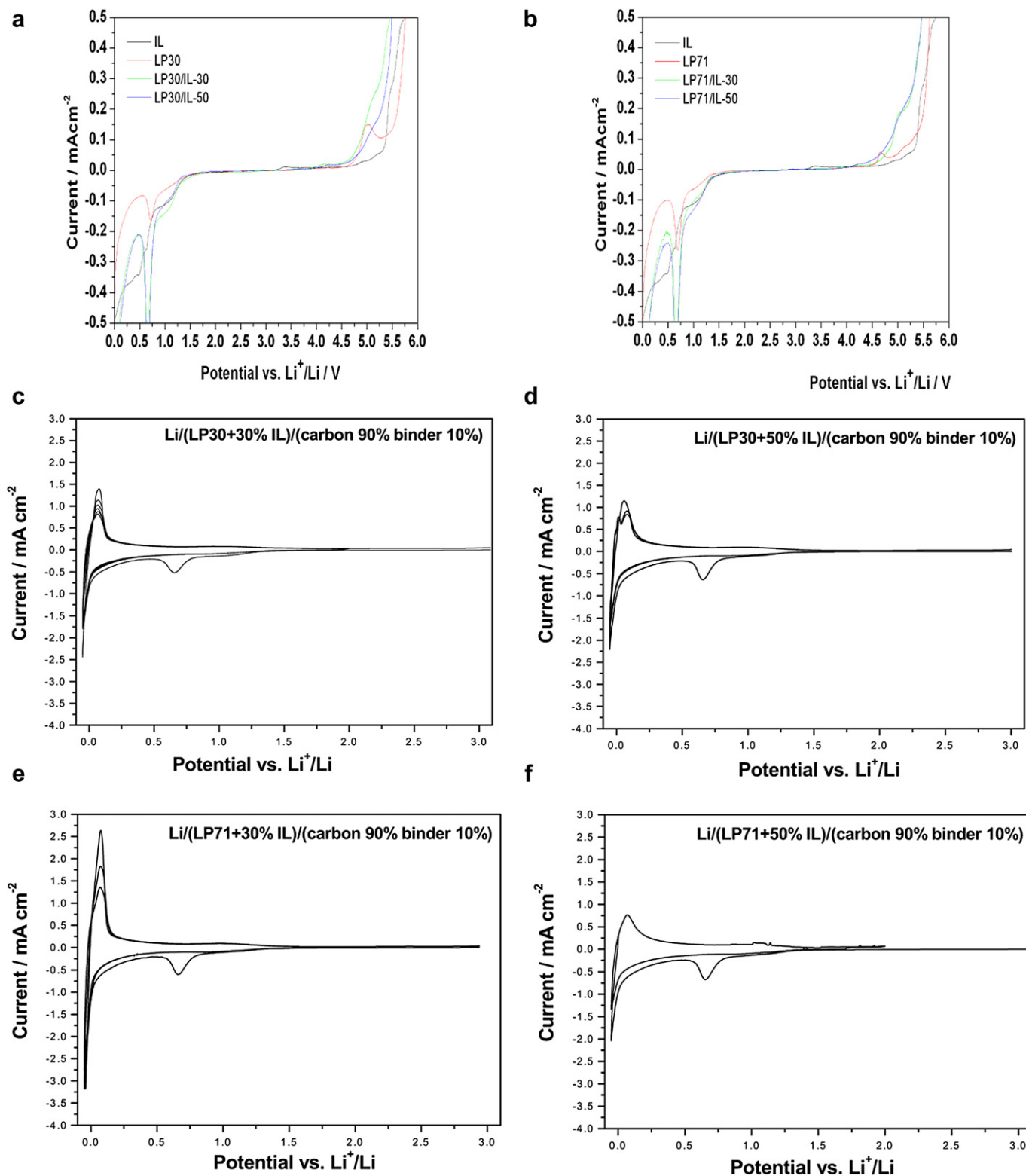
The thermal stability of the solutions was investigated by flammability tests. Few drops of the samples were placed on a watch glass and exposed to a burner for 3 s to allow ignition. The time required to extinguish the flame was recorded and normalized against liquid mass to evaluate the self-extinguish time (SET) in s g<sup>−1</sup> [22].

Cyclic cathodic voltammetry measurements and linear anodic scans were performed to evaluate the electrochemical stability window of all the solutions. Measurements were carried out by using home-made, “T-type” polyethylene cells with “SuperP” carbon (MMM Belgium) casted on copper or aluminum as working electrode and two lithium foils (Chemetall) as counter and reference electrodes. Cell was scanned in the 3.0–0 V (cathodic scan) and 3.0–6.0 V (anodic scan) voltage ranges at a scan rate of 0.2 mV s<sup>−1</sup> by using a VMP Biologic-Science Instruments [27–29].

**Fig. 1.** Arrhenius plot of (a) LP30-based and (b) LP71-based electrolytes compared to pure IL.

The cells for galvanostatic tests were assembled by coupling a lithium metal foil anode with a  $\text{LiFePO}_4$  cathode (LFP), using the selected solution soaked in a Whatman<sup>TM</sup> separator as electrolyte. The same electrolytes were also tested in a different cell

configuration by coupling a lithium foil and a  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode (LTO). The electrodes were prepared by doctor-blade deposition on aluminum substrate of a slurry formed of 80% active material ( $\text{LiFePO}_4$  kindly provided by Dr. Margret Wohlfahrt-Mehrens of



**Fig. 2.** Electrochemical stability window of (a) LP30-based and (b) LP71-based electrolytes compared to pure IL; (c-d-e-f) cathodic cyclic voltammograms of the mixtures of  $\text{Py}_{14}\text{TFSI}$  with LP30 or LP71.

ZSW, Ulm, Germany, or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Altairnano product), 10% PVDF 6020 Solvay Solef (binder) and 10% SP carbon. All the tested electrodes, SuperP-, LFP- or LTO-based, were all casted in air and dried at 100 °C in a vacuum oven overnight ( $p \sim 0.1\text{--}1$  mbar); the electrode film was then punched in 10 mm diameter round disks: the latter were dried under vacuum ( $<10^{-2}$  mbar) for 3–6 h at 110 °C and then stored directly into an Ar-filled glove box without further exposition with air. “T-type” cell hardware was used to perform these electrochemical tests on lithium half-cells and Li-ion cells.

The LFP or LTO lithium cells were tested by galvanostatic cycling in a 2.2–4.5 V and in a 1.0–2.5 V voltage ranges, respectively, by using a Maccor Series 4000 Battery Test System. All cells were cycled at C/5 rate (1 C current being  $0.223\text{ A g}^{-1}\text{ cm}^{-2}$  with respect to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  active mass and  $0.217\text{ A g}^{-1}\text{ cm}^{-2}$  with respect to  $\text{LiFePO}_4$  active mass). The performance of each cell was evaluated in terms of specific capacity, charge/discharge efficiency and cycle life.

A lithium-ion cell was assembled by coupling a  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode with a  $\text{LiFePO}_4$  cathode with a selected electrolyte solution, i.e. LP30/Py<sub>14</sub>TFSI 70/30 wt/wt., soaked in a Whatman™ separator. The complete Li-ion cell was tested by galvanostatic cycling in a 0.2–2.3 V voltage range at C/5 rate (1 C current being  $0.223\text{ A g}^{-1}\text{ cm}^{-2}$  with respect to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  active mass). The cell was anode-limited and the positive to negative electrodes weights ratio was  $P/N = 1.5$ .

### 3. Results and discussion

The Arrhenius plots of the LP30-based and the LP71-based solutions are shown in Fig. 1a and b compared to the pure Py<sub>14</sub>TFSI ionic liquid. The conductivity of the ionic liquid ranges between  $10^{-3}$  and  $10^{-2}\text{ S cm}^{-1}$  in the entire temperature range i.e. from 15 °C to 60 °C: this value is suitable for lithium-ion battery applications [30]. The addition of the ionic liquid to the commercial electrolyte solutions does not reduce the overall ionic conductivity neither for LP30 nor for LP71. In fact, although the large added amounts of ionic liquid (30–50%), the conductivity values of the

**Table 2**

Flammability test: sample initial weight, flame exposure time, flame extinguish time and self extinguishing time (SET) of LP30, LP30/Py<sub>14</sub>TFSI 70/30 wt/wt, LP30/Py<sub>14</sub>TFSI 50/50 wt/wt.

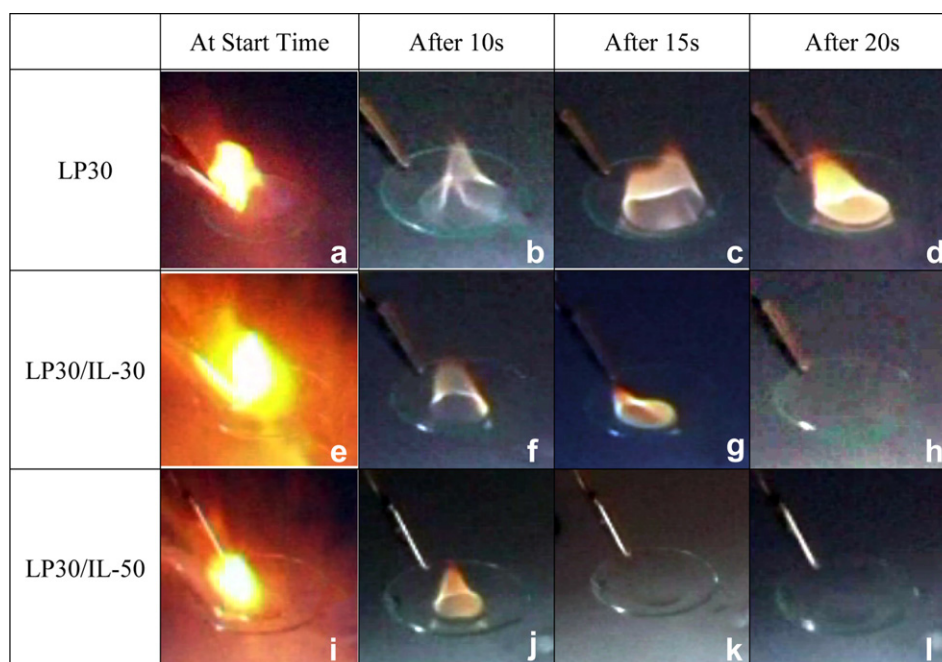
	LP30	LP30/IL-30	LP30/IL-50
Sample initial weight	0.508 g	0.4826 g	0.4844 g
Flame exposure time	3 s	3 s	3 s
Flame extinguish time	22.86 s	17.11 s	12.94 s
Self-extinguishing time (SET)	45.00 s g <sup>-1</sup>	35.45 s g <sup>-1</sup>	26.71 s g <sup>-1</sup>

mixtures are very similar to the LP30 or LP71 pure solutions and approximately 5 times larger in comparison to the IL. Slightly higher conductivity values are obtained in the case of LP30-based solutions, with respect to LP71-based electrolytes.

The electrochemical stability windows of all the investigated solutions are reported in Fig. 2a and b. These plots were built by adding the experimental results obtained in cathodic cyclic voltammetry and anodic linear sweep voltammetry tests [31]. Only the first anodic and cathodic scans are here reported. The steady current–voltage response of the SuperP carbon electrodes shows that the addition of the ionic liquid slightly improves the stability window of all the mixed solutions.

To be noticed that pure IL shows the highest stability at high voltage. The pre-decomposition peaks that are observed in pure alkylcarbonates solutions at about 4.6 V for LP71 and 4.8 V for LP30 (see Fig. 2a and b), are absent in all the mixed electrolytes and the current drift is slightly shifted toward higher voltage.

It is interesting to observe that the typical poor cathodic stability of conventional imidazolium-based ILs [7] are partially overcome by the choice of a suitable pyrrolidinium cation having no highly acidic protons. Indeed, the small current drift observed around 1.5 V vs.  $\text{Li}^+/\text{Li}$  for pure Py<sub>14</sub>TFSI decreases in subsequent cathodic cycles (here not reported): it is likely due to a multi-step decomposition process, resulting in the formation of a protective passivation film [18–29]. Therefore, due to the occurrence of a solid–electrolyte interface film (SEI), we conclude that the cathodic stability of Py<sub>14</sub>TFSI can be kinetically extended well below 1.5 V.



**Fig. 3.** Pictures of the flammability performances of LP30 at starting time (a), after 10 s (b), after 15 s (c) and after 20 s (d), LP30/Py<sub>14</sub>TFSI 70/30 wt/wt at starting time (e), after 10 s (f), after 15 s (g) and after 20 s (h) And LP30/Py<sub>14</sub>TFSI 50/50 wt/wt at starting time (i), after 10 s (j), after 15 s (k) and after 20 s (l).



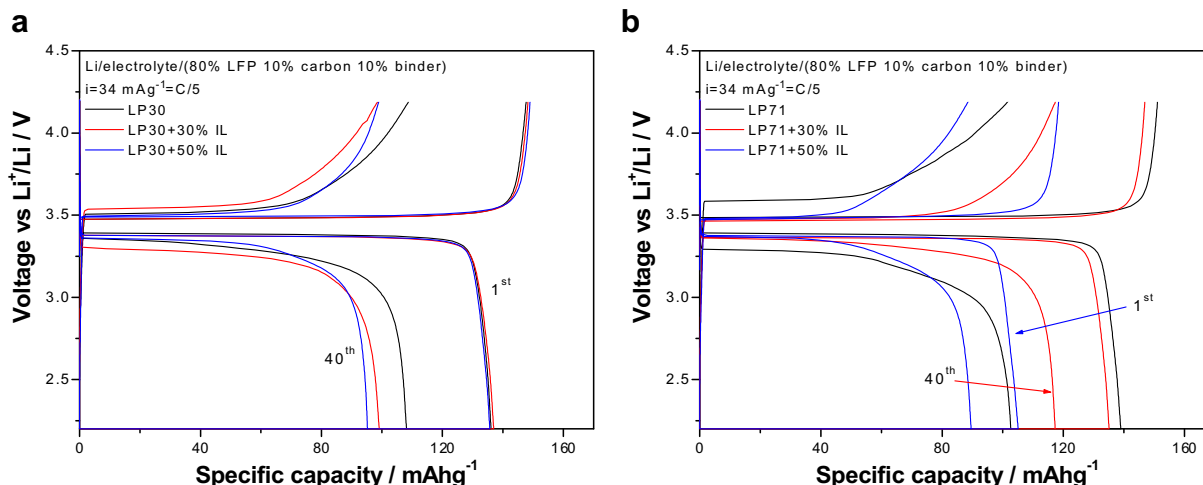


Fig. 4. Voltage (vs.  $\text{Li}^+/\text{Li}$ ) vs. specific capacity (cycles 1 and 40) for (a) the Li/LP30-based electrolyte solution/ $\text{LiFePO}_4$  and (b) Li/LP71-based electrolyte solution/ $\text{LiFePO}_4$  cells.

This occurs also on the IL-carbonate mixture electrolytes (see Fig. 2c–f) due to the formation of the stable film typically observed on EC-based electrolytes. In fact the stable passivation of the electrodes upon reduction is nicely confirmed by the CV cycles besides the first discharges. The charge irreversibly consumed in the first discharges below 1.5 V (but mainly at 0.7–0.8 V) is not observed in the subsequent cycles for all the studied electrolytes. It is to be noted that Appetecchi et al. [8] observed that the pure  $\text{Py}_{14}\text{TFSI}$  ionic liquid is more stable cathodically than our results. In particular the small drift current observed at a potential of approximately 1.5 V vs.  $\text{Li}^+/\text{Li}$  is not observed by Appetecchi and co-workers [8]. However the experimental conditions are different and therefore the corresponding experimental results are not easily comparable [7,8]. We determined the stability windows by using carbonaceous working electrodes (superP carbon versus lithium metal) and Li metal as reference electrode. These working electrodes are made with high surface area non graphitic carbon nanoparticles in order to enhance any parasitic decomposition due to electrolyte degradation. The parasitic decomposition reactions were also enhanced by using a slow scan rate ( $0.2 \text{ mV s}^{-1}$ ). In literature similar tests are usually done using platinum or glassy carbon flat working electrodes versus carbon paper (and Ag inert reference electrodes) with fast scan rates (e.g.  $5\text{--}10 \text{ mV s}^{-1}$ ) thus minimizing any electroactive process [7,8]. In this view our tests are much severe with respect to the literature.

The addition of the IL to the standard electrolytes results in large improvements of the response to flammability tests (see Fig. 3; results for the LP71-cases are very similar and are therefore omitted to avoid redundancy). When exposed to a free flame the LP30 electrolyte still burns after 20 s whereas the flame on samples containing 30% in weight of the ionic liquid extinguished within 20 s (Fig. 3h) and within 15 s in the case of samples containing 50% in weight of ionic liquid. Details on flammability test and the estimated values of the self extinguish time for the LP30-based solutions are summarized in Table 2. Briefly, by increasing the amount of ionic liquid in the sample, the self-extinguishing time (SET, i.e. the flame extinguish time normalized to the weight of the samples) strongly decreases, thus highly improving safety. This effect is expected as pure  $\text{Py}_{14}\text{TFSI}$  is non-flammable.

The four mixed electrolytes have been galvanostatically tested in lithium cells vs.  $\text{LiFePO}_4$  and compared with benchmark cells assembled with pure LP30 and LP71 electrolytes. The charge/discharge voltage profiles (1st and 40th cycles) are reported in Fig. 4a and b for the LP30-based and LP71-based electrolytes, respectively. The specific capacity plots vs. cycle number are reported for the first forty cycles in Fig. 5a and b for the LP30-based and LP71-based electrolytes, respectively. The addition of the ionic liquid to both the standard electrolytes, i.e. LP30 and LP71, apparently does not affect the performances of the electrode active material in terms of specific capacity, reversibility and cyclability.

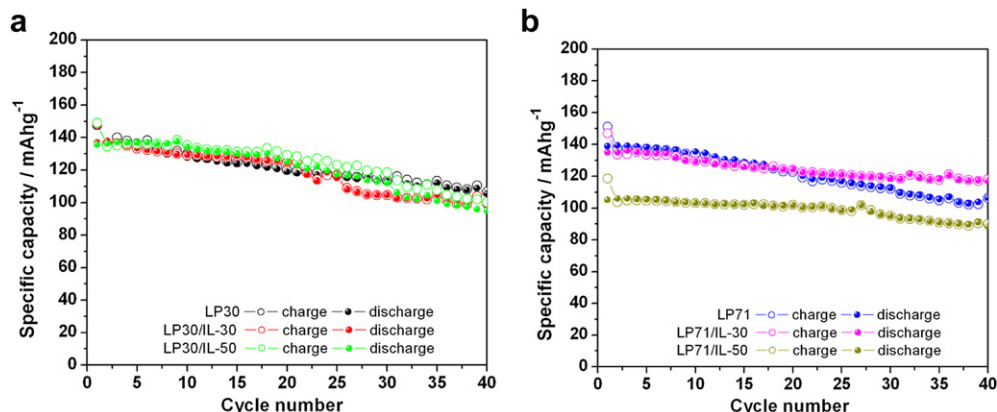
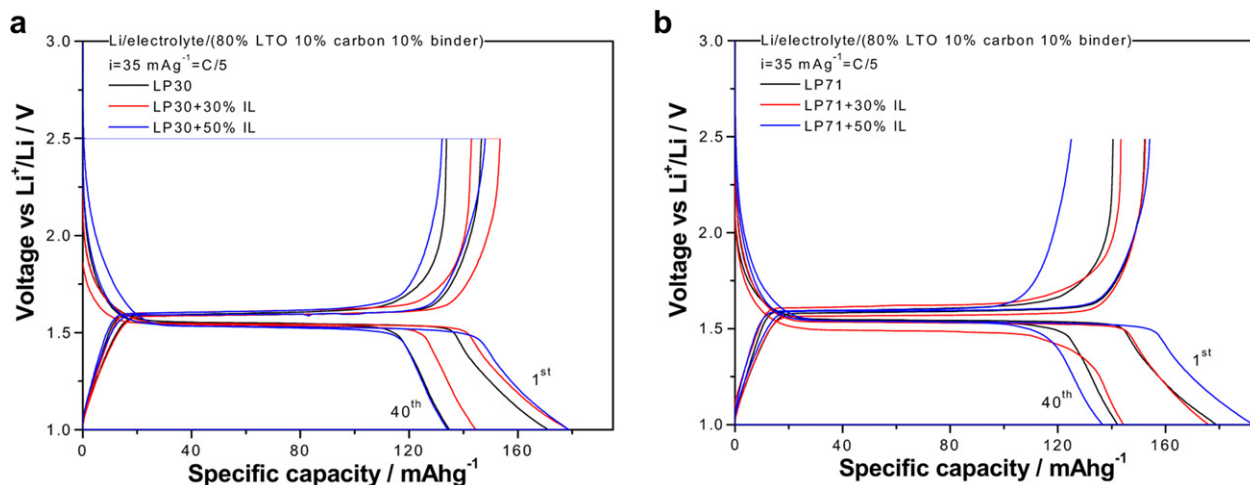


Fig. 5. Specific capacity vs. cycle number for (a) the Li/LP30-based electrolyte solution/ $\text{LiFePO}_4$  and (b) the Li/LP71-based electrolyte solution/ $\text{LiFePO}_4$  cells.



**Fig. 6.** Voltage (vs.  $\text{Li}^+/\text{Li}$ ) vs. specific capacity (cycles 1 and 40) for (a) the Li/LP30-based electrolyte solution/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and (b) the Li/LP71-based electrolyte solution/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$  cells.

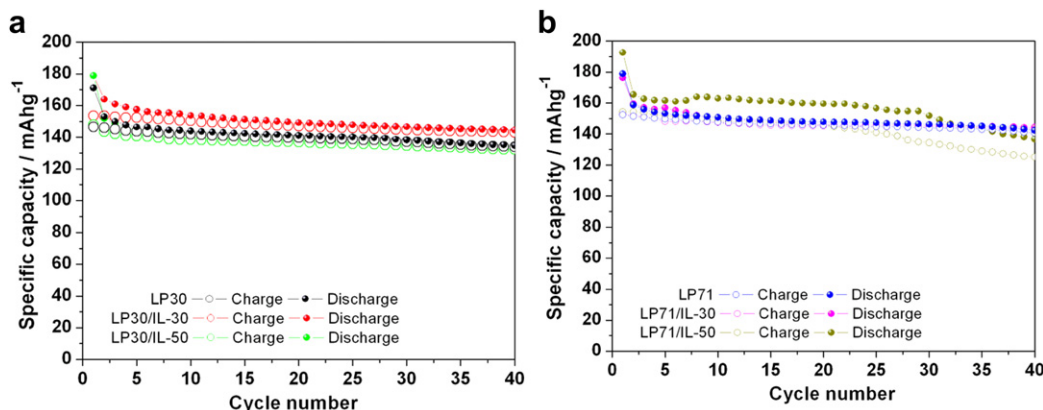
In particular the electrolytes LP30/ $\text{Py}_{14}\text{TFSI}$  70/30 wt/wt and LP71/ $\text{Py}_{14}\text{TFSI}$  70/30 wt/wt show negligible differences in performances with respect to the pure alkylcarbonate electrolytes. Only in the case of LP71/ $\text{Py}_{14}\text{TFSI}$  50/50 wt/wt a clear decrease of the cycled specific capacity is observed from the first cycle (–23% specific capacity in the first cycle compared to pure LP71 with a capacity retention of 83% at cycle 40 to be compared to 69% for pure LP71). This experimental evidence, that has been confirmed in triplicate, suggests that at such high concentration of IL the nature of the alkylcarbonate mixture plays a key role in the stabilization/destabilization of the electrode–electrolyte interphase, even at potentials well within the stability window of the electrolyte mixture.

A similar study has been also performed for all the four mixed electrolytes in lithium cells vs.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . Galvanostatic cycling has been performed, in comparison with benchmark cells assembled with pure LP30 and LP71 electrolytes. The charge/discharge voltage profiles (1st and 40th cycles) are reported in Fig. 6a and b for the LP30-based and LP71-based electrolytes, respectively. The specific capacity vs. cycle number is reported, for the first forty cycles, in Fig. 7a and b for the LP30-based and LP71-based electrolytes, respectively. Also the galvanostatic tests in lithium cells vs. lithium titanate confirm that the addition of the ionic liquid to both the standard solutions, i.e. LP30 and LP71 does not affect the performances in terms of specific capacity, reversibility and cyclability. Similarly to the  $\text{LiFePO}_4$  case,

a remarkable worsening of the performances is observed in the case of LP71/ $\text{Py}_{14}\text{TFSI}$  50/50 wt/wt electrolyte. This effect has been confirmed by testing three different batches of the same electrolyte. This evidence supports the above mentioned hypothesis: the nature of the alkylcarbonate mixture, and in particular the presence of DEC, strongly affect the interphase stability at high concentration of IL.

For a deeper understanding of this aspect, further investigations such as in-situ XRD analysis and ex-situ Raman IR spectroscopic characterization are currently in progress in order to elucidate structural features of the solid electrolyte interphases under working conditions, as well as to define the molecular interactions among the various components of the mixture electrolytes. The results of this study will be reported in a future publication.

With reference to Figs. 4 and 6a and b, it's remarkable that the voltage hysteresis in the firsts cycles between charge and discharge is only marginally affected for both LFP and LTO lithium cells when passing from 30 to 50 wt.% of the ionic liquid. An estimation of the voltage hysteresis ( $\Delta V$ , calculated as the difference between the voltage related to the charge plateau and that related to the discharge one) is reported for the 1st, the 5th and the 40th cycles of all the 12 cells in the [Supplementary material \(Tables A and B\)](#); demonstrating that the increase of  $\Delta V$  in the first cycles is limited to less than 20 mV with the addition of the IL. After 40 cycles the voltage hysteresis grows in all cases: in the case of the LTO cells the growth is apparently more limited in respect to the LFP cells.



**Fig. 7.** Specific capacity vs. cycle number for (a) the Li/LP30-based electrolyte solution/and (b) the Li/LP71-based electrolyte solution/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$  cells.

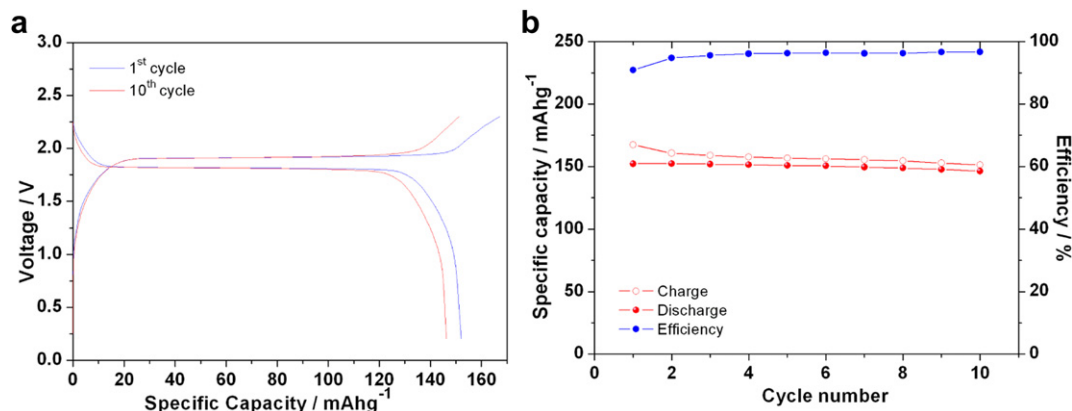


Fig. 8. (a) Cell voltage vs. specific capacity and (b) specific capacity vs. cycle number for the LiFePO<sub>4</sub>/LP30/Py<sub>14</sub>TFSI 30/70 wt/wt/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> lithium-ion cell.

To be noticed that specific capacities achieved for the investigated cells are always slightly lower than the theoretical values (assumed to be 170 mAh g<sup>-1</sup> for LiFePO<sub>4</sub> and 175 mAh g<sup>-1</sup> for Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>), including the case of cells adopting pure LP30 and LP71 reference electrolytes. Being the scope of the present paper a comparative investigation of different electrolyte compositions, the issue of absolute cell performance is beyond the scope of this work.

Applicability of IL-added solutions was also confirmed by cycling a complete lithium-ion cell. The studied Li-ion cell has been assembled by coupling the LiFePO<sub>4</sub> cathode and the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode and one of the mixed electrolyte. Among those investigated, mixtures containing 30 wt.% of IL appeared the best choice, showing capacity values in lithium metal cells comparable, or even better, than the pure, IL-free electrolyte. Thus, LP30/Py<sub>14</sub>TFSI 70/30 wt/wt was selected, based on its enhanced conductivity with respect to LP71/Py<sub>14</sub>TFSI 70/30 wt/wt. The origin of this superior behavior is rooted in the fundamental chemistry that drives the changes of the conductivities, variation of the stability windows and ability to sustain galvanostatic cycling, and it is beyond the scope of this paper. The voltage profiles vs. the specific capacity of first and tenth cycles of the assembled lithium-ion cell is shown in Fig. 8.

This final test has been carried out in order to demonstrate the ability of these electrolytes to be successfully used in complete Li-ion cells thus drastically increasing the safety of the overall device.

#### 4. Conclusions

Four electrolytes for Li-ion cells have been developed by adding large amounts (up to 50 wt.%) of an ionic liquid, i.e. *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Py<sub>14</sub>TFSI) to conventional alkylcarbonate-based electrolyte solutions (LP30 and LP71). The mixed electrolytes show conductivity values comparable to the pure carbonate-based electrolyte solutions, improved electrochemical stability windows and a large reduction of the SET when exposed to a free flame. With the exception of the LP71/Py<sub>14</sub>TFSI 50/50 wt/wt mixture, the mixed IL-carbonate electrolytes show good performances in lithium cells vs. LTO and LFP.

A LFP–LTO Li-ion cell has been assembled and tested thus demonstrating the use of one of these mixed electrolytes in a complete device with a drastically improved safety profile.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2012.11.017>.

#### References

- [1] B. Scrosati, Chem. Rec. 5 (2005) 286.
- [2] B. Scrosati, J. Garche, J. Power Sources 195 (2010) 2419.
- [3] S. Brutti, V. Gentili, H. Menard, B. Scrosati, P.G. Bruce, Adv. Energy Mater. 2 (2012) 322–327.
- [4] S. Brutti, V. Gentili, P. Reale, L. Carbone, S. Panero, J. Power Sources 196 (2011) 9792–9799.
- [5] H. Ohno, Electrochemical Aspects of Ionic Liquids, Wiley, New York, 2005.
- [6] A. Farnicola, B. Scrosati, H. Ohno, Ionics 12 (2006) 95.
- [7] M. Galinski, A. Lewandowski, I. Stepniak, Electrochim. Acta 51 (2006) 5567.
- [8] G.B. Appetecchi, S. Scacia, C. Tizzani, F. Alessandrini, S. Passerini, Electrochem. Soc. 153 (2006) A1685.
- [9] P.C. Howlett, D.R. MacFarlane, A.F. Hollenkamp, Electrochem. Solid State Lett. 7 (2004) A97.
- [10] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, N. Kihira, M. Watanabe, N. Terada, J. Phys. Chem. B 110 (2006) 10228.
- [11] J. Salminen, N. Papiconomou, R.A. Kumar, J.-M. Lee, J. Kerr, J. Newman, J.M. Prausnitz, Fluid Phase Equilib. 261 (2007) 421.
- [12] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, J. Phys. Chem. B 103 (1999) 4164.
- [13] D.R. MacFarlane, J. Sun, J. Golding, P. Meakin, M. Forsyth, Electrochim. Acta 45 (2000) 1271.
- [14] M. Armand, F. Endres, D.F. MacFarlane, H. Ohno, B. Scrosati, Nat. Mater. 8 (2009) 621.
- [15] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 160 (2006) 1308.
- [16] B. Garcia, S. Laval, G. Perron, C. Michot, M. Armand, Electrochim. Acta 49 (2004) 4583.
- [17] A. Farnicola, F. Croce, B. Scrosati, T. Watanabe, H. Ohno, J. Power Sources 41 (2007) 348.
- [18] J. Hassoun, A. Farnicola, M.A. Navarra, S. Panero, B. Scrosati, J. Power Sources 195 (2010) 574.
- [19] P. Reale, A. Farnicola, B. Scrosati, J. Power Sources 194 (2009) 182.
- [20] M.A. Navarra, J. Manzi, L. Lombardo, S. Panero, B. Scrosati, ChemSusChem 4 (2011) 125.
- [21] A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagacé, A. Vijh, K. Zaghib, J. Power Sources 195 (2010) 845.
- [22] C. Arbizzani, G. Gabrielli, M. Mastragostino, J. Power Sources 196 (2011) 4801.
- [23] P.M. Bayley, G.H. Lane, N.M. Rocher, B.R. Clare, A.S. Best, D.M. MacFarlane, M. Forsyth, Phys. Chem. Chem. Phys. 11 (2009) 7202.
- [24] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.
- [25] L. Larush, V. Borgel, E. Markevich, O. Haik, E. Zinigrad, D. Aurbach, G. Semrau, M. Shmidt, J. Power Sources 189 (2009) 217.
- [26] D. Aurbach, I. Weissman, A. Zaban, P. Dan, Electrochim. Acta 45 (1999) 1135.
- [27] S. Megahed, B. Scrosati, Interface 4 (1995) 34.
- [28] J.L. Nowinski, P. Lightfoot, P.G. Bruce, J. Mater. Chem. 4 (1994) 1579.
- [29] P.C. Howlett, N. Brack, A.F. Hollenkamp, M. Forsyth, D.R. MacFarlane, J. Electrochem. Soc. 153 (2006) A595.
- [30] J. Barthel, H.J. Gores, in: J.O. Besenhard (Ed.), Handbook for Battery Materials, Wiley-VCH, Weinheim, 1999, p. 457.
- [31] C. Sirisopanaporn, A. Farnicola, B. Scrosati, J. Power Sources 19 (2009) 490.